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Investigations on Some Divalent Transition Metal Complexes of 10-Membered Tellurium Containing N_2S_2 Donor Macrocycles

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Abstract

A new series of complexes has been synthesized by template condensation of 2-aminoethanthiol and diaryltellurium dichlorides, R_2TeCl_2 (R=*p*-hydroxyphenyl and 3-methyl-4-hydroxyphenyl) in methanolic medium in the presence of divalent metal chlorides forming complexes of the type [ML^1Cl_2] and [ML^2Cl_2] where [M=Mn (II), Co (II) and Cu (II); L^1 and L^2=10-membered tellurium containing dithiadiaza macrocyclic ligands]. On the basis of elemental analyses, conductance, magnetic moment measurements, ^{1}HNMR, Infrared and electronic absorption spectroscopy their structures have been elucidated. Based on these studies, a six coordinate octahedral geometry for these complexes have been proposed. These metal complexes have also been screened for their antimicrobial activity against some pathogenic bacteria and fungi.

***Keywords:** 2-Aminoethanethiol; Antimicrobial activity; Octahedral geometry; Tellurium containing dithiadiaza macrocycles*

Introduction

Coordination chemistry of organotellurium ligands containing hard donors such as nitrogen and oxygen along with soft tellurium is quite interesting as such ligand framework can provide insight into a competitive coordination behaviour between the hard and soft donors towards the metal center [1,2]. Some macrocyclic complexes have received special attention due to their mixed hard-soft donor character and versatile coordination behavior [3] and also due to their pharmacological properties [4].

The macrocyclic complexes have various applications such as dyes and pigments [5], biological activity [4,6,7], precursors in MOCVD processes [8-10], models for biologically important proteins and enzymes [11-16]. Template synthetic route for transition metal complexes of dithiadiaza 16 and tellurium containing tetraaza [17-21] macrocycles have been reported. Due to the growing interest in macrocyclic metal complexes and in continuation of our earlier research work [22,23] we herein report the synthesis, characterization and antimicrobial activity of some 10-membered tellurium containing dithiadiaza macrocyclic complexes of divalent cobalt, manganese and copper.

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Materials and Methods

The chemicals used for synthesis and recrystallization were of reagent grade. The solvents, phenol and *o*-cresol were purified and dried by standard methods [24,25] before use. All the preparations were carried out under an atmosphere of dry nitrogen as the compounds are sensitive to moisture and air.

Preparation of diaryltellurium dichlorides

Bis (3-methyl-4-hydroxyphenyl) and bis (p-hydroxyphenyl) tellurium dichlorides were prepared by reactions of tellurium tetrachloride with o-cresol [26] and phenol [27] respectively, as reported in the literature.

Preparation of metal complexes with 10-membered tellurium dithiadiaza macrocycles (Te_2N_2 S_2M system)

The metal complexes were synthesized by template condensation of diaryltellurium dichlorides and 2-aminoethanthiol in presence of divalent metal chlorides in 2:2:1 molar ratios, as per the procedure given below:

A hot saturated solution (4.0 mmol) of diaryltellurium dichloride in dry methanol was added dropwise with constant stirring to a hot solution (4.0 mmol) of 2-aminoethanthiol in methanol taken in a round bottom flask. An immediate change in colour was observed. The contents were refluxed for 4-5 h, followed by the addition of hot saturated methanolic solution of divalent metal chlorides (2.0 mmol). Again, a change in colour was observed. The mixture was then further refluxed for about 7-8 h. This was kept in refrigerator after concentrating to about one third of original volume to obtain the crystalline coloured product. This was filtered, washed with petroleum ether and dried in vacuum desiccator over P_4O_{10}.

Physical studies

Conductance was measured in acetonitrile at 25 ± 2°C using a dip type conductivity cell (cell constant=0.997) on a microprocessor based conductivity bridge type MICROSIL. Electronic spectra were recorded on a UV-VIS-NIR Spectrophotometer; model UV-3600 Plus (SHIMADZU) in $BaSO_4$ at 25 ± 2°C. Magnetic mass susceptibility data were obtained from NPL, New Delhi on a Gouy’s balance (model Johnson Matthey Alfa products) using glycerin as a calibrant. IR (4000 cm^{-1}-400 cm^{-1}) spectra were recorded on Brucker (Alpha), software; OPUS 7.2.139.1294 Spectrometer.

^1H NMR Spectra were obtained from SAIF, Panjab University, Chandigarh on BRUKER AVANCE II 400 NMR spectrometer in DMSO-d_6 using TMS as reference. C, H, N analyses for these metal complexes were obtained from SAIF, Panjab University, Chandigarh on a Microprocessor based Thermo Scientific (FLASH 2000) CHN Elemental Analyser. Chlorine and tellurium contents were determined volumetrically [28] while cobalt and manganese gravimetrically [28]. Atomic absorption spectrophotometer (ECIL Model No.4129) was used to estimate copper.

Antimicrobial screening

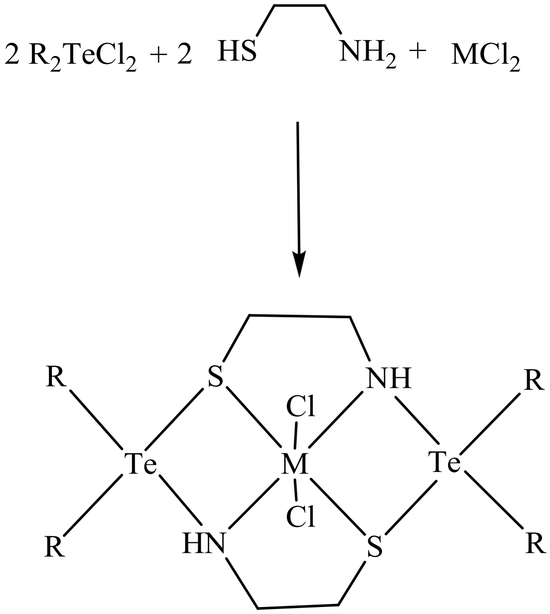
The antifungal and antibacterial activity of the synthesized macrocyclic metal complexes and their precursors were tested against fungal strains: *Candida albicans* (MTCC 227), *Aspergillus niger* (MTCC 8189) and *Aspergillus fumigatus* (ITCC 4517); Gram +ve bacteria: *Staphylococcus aureus* (MTCC 2901), *Bacillus subtilis* (MTCC 2063) and *Bacillus cereus* (MTCC 7350) and Gram -ve bacteria: *Escherichia coli* (MTCC 1652) and *Salmonella typhi* (ATCC 15499) using tube dilution method [29] The test and standard compounds were both serially diluted in double strength nutrient broth I.P for bacteria and Sabouraud Dextrose Broth –I.P for fungi [30]. Fluconazole (antifungal) and Cefadroxil (antibacterial) were taken as standard drugs.

Results and Discussion

When tellurium tetrachloride is heated with arene, R-H (*o*-cresol and phenol) gives corresponding diaryltellurium dichlorides [26,27] as per the equation:

$$2\ R\text{-}H + TeCl_2 \rightarrow R_2\ TeCl_2 + 2\ HCl$$

These diaryltellurium dichlorides when heated with 2-aminoethanthiol in presence of $CoCl_2.6H_2O/CuCl_2/MnCl_2.4H_2O$ in 2:2:1 molar ratios yield the desired complexes as shown in SCHEME 1.



L1; R=p-hydroxyphenyl

L2; R=3-methyl-4-hydroxyphenyl

SCHEME 1. **Formation Co (II), Mn (II) and Cu (II) complexes.**

The analytical data for these complexes are presented in TABLE 1. These newly synthesized metal complexes are colored, crystalline solids which are stable in dry air and soluble in polar donor organic solvents.

Conductance measurement

The molar conductance values for Co (II) and Mn (II) complexes in DMSO at *ca.* 10^{-3} M are lower than the ranges reported [31] for 1:1 type electrolytes. These values reflect the partial dissociation of these complexes in this solvent. The molar conductance for CuL^2Cl_2 is close to those of 1:1 electrolytes and for CuL^1Cl_2 is higher than those of 1:1 type electrolytes. These two complexes probably ionize into $[CuLCl.DMSO]^+$ and Cl^- ions due to the solvation process, since DMSO is known to be a good donor. So, on the basis of conductance studies, these complexes in general may be represented as $[MLCl_2]$.

TABLE 1. **Analytical data and physical properties for metal complexes.**

Complex	**Empirical formula (FW)**	**Colour (Yield, %)**	**M.P. °C**	**Analysis found (calculated), %**						**$\wedge_M$ at *ca.*10^{-3} M Scm^2 mol^{-1} in DMSO**
				C	**H**	**N**	**Cl**	**Te**	**M**	
[CoL^{1}Cl$_2$]	$C_{28}H_{30}Cl_2N_2O_4S_2Te_2Co$ (907.72)	Green (76)	140-142	36.88 (37.05)	3.51 (3.33)	2.88 (3.09)	7.31 (7.81)	27.88 (28.11)	6.12 (6.49)	37.7
[MnL^{1}Cl$_2$]	$C_{28}H_{30}Cl_2N_2O_4S_2Te_2Mn$ (903.72)	Light yellow (80)	120-122	37.01 (37.21)	3.04 (3.35)	2.89 (3.10)	7.50 (7.85)	28.01 (28.24)	5.88 (6.08)	26.4
[CuL^{1}Cl$_2$]	$C_{28}H_{30}Cl_2N_2O_4S_2Te_2Cu$ (927.37)	Blue (68)	152-154	37.79 (37.56)	3.33 (3.59)	2.88 (3.02)	7.42 (7.65)	27.96 (27.52)	6.66 (6.85)	92.9
[CoL^{2}Cl$_2$]	$C_{32}H_{38}Cl_2N_2O_4S_2Te_2Co$ (963.82)	Dark green (70)	142-144	39.54 (39.88)	3.79 (3.97)	2.75 (2.91)	7.01 (7.36)	26.17 (26.48)	5.87 (6.11)	41.3
[MnL^{2}Cl$_2$]	$C_{32}H_{38}Cl_2N_2O_4S_2Te_2Mn$ (959.83)	Brown (81)	135-137	39.80 (40.04)	4.12 (3.99)	2.68 (2.92)	7.12 (7.39)	26.78 (26.59)	5.44 (5.72)	29.2
[CuL^{2}Cl$_2$]	$C_{32}H_{38}Cl_2N_2O_4S_2Te_2Cu$ (968.44)	Light green (74)	110-112	39.34 (39.69)	3.76 (3.96)	2.61 (2.89)	7.14 (7.32)	26.10 (26.35)	6.25 (6.56)	53.6

Magnetic moment and electronic spectra

The electronic absorption and magnetic moment data for the complexes are presented in TABLE 2. Co (II) complexes show magnetic moment 4.65-4.81 B.M. corresponding to three unpaired electrons. Electronic spectrum shows bands at 9398 cm^{-1}–9890 cm^{-1}, 14992 cm^{-1}–15649 cm^{-1} and 32362 cm^{-1}–32530 cm^{-1}, which may be assigned to the transitions from $^4T_{1g} \rightarrow {}^4T_{2g}$ (F), $^4T_{1g} \rightarrow {}^4A_{2g}$ (F) and $^4T_{1g}$ (F)$\rightarrow$ $^4T_{1g}$ (P) and CT, respectively. The electronic spectral pattern suggests octahedral geometry[18,19,32-34] of Co (II) complexes.

TABLE 2. **Magnetic moment and electronic spectral data for metal complexes.**

Complex	**Band position (cm^{-1})**	**Assignments**	**Observed magnetic moment (B.M.)**
[CoL^{1}Cl$_2$]	9890 14992 32530	$^4T_{1g} \rightarrow {}^4T_{2g}$ (F) $^4T_{1g} \rightarrow {}^4A_{2g}$ (F) $^4T_{1g}$(F) $\rightarrow$ $^4T_{1g}$ (P) and CT	4.65
[MnL^{1}Cl$_2$]	24390 35299	$^6A_{1g} \rightarrow {}^4A_{1g}$ (G) $^6A_{1g} \rightarrow {}^4A_{2g}$ (F) and CT	5.62
[CuL^{1}Cl$_2$]	12500 26666 33333	$^2B_{1g} \rightarrow {}^2A_1g$ $^2B_{1g} \rightarrow {}^2B_2g$ CT	2.16
[CoL^{2}Cl$_2$]	9398 15649 32362	$^4T_{1g} \rightarrow {}^4T_{2g}$ (F) $^4T_{1g} \rightarrow {}^4A_{2g}$ (F) $^4T_{1g}$(F)$\rightarrow$ $^4T_{1g}$ (P) and CT	4.81
[MnL^{2}Cl$_2$]		$^6A_{1g} \rightarrow {}^4A_{1g}$ (G)	5.82

	24096 34965	$^6A_{1g} \rightarrow {}^4A_{2g}$ (F) and CT	
[CuL^{2}Cl$_2$]	12562-32467	$^2B_{1g} \rightarrow {}^2A_1g$ $^2B_{1g} \rightarrow {}^2B_2g$ CT	1.80

The Mn (II) complexes show magnetic moment corresponding to five unpaired electrons (5.62-5.82 B.M.) at room temperature close to the spin only value of 5.92 B. M. Electronic spectra exhibit two weak absorption bands as shown in TABLE 3, which are characteristics of octahedral geometry [18,19,21,32-34].

TABLE 3. **Important IR Data (cm^{-1}) for metal complexes.**

Complex	ν_{N-H}	**N-H def.**	**N-H out of plane bending**	ν_{C-N}	ν_{C-S}	ν_{M-N}	ν_{M-S}	ν_{M-Cl}	ν_{Te-N}
[CoL^{1}Cl$_2$]	3200 m	1625 m	826 s	1172 s	756 w	472 w	338 w	302 w	404 w
[MnL^{1}Cl$_2$]	3162* s	1629 s	826 s	1172 s	755 m	510 w	328 w	328 m	436 w
[CuL^{1}Cl$_2$]	3121 s b	1615 s	825 s	1173 s	758 m	510 w	325 w	331 w	418 w
[CoL^{2}Cl$_2$]	3173 s	1622 m	811 s	1175 m	759 m	475 w	349 w	314 w	410 w
[MnL^{2}Cl$_2$]	3100 s	1633 s	811 s	1176 m	763 m	516 w	339 w	329 w	434 w
[CuL^{2}Cl$_2$]	3120 m	1651 s	812 s	1175 m	759 m	460 w	321 w	321 w	434 w
m: Medium, b: Broad, s: Strong, w: Weak, *Mixed with ν_{O-H}									

Cu (II) complexes show magnetic moment in the range 1.80-2.16 B.M. at room temperature corresponding to one unpaired electron. In these complexes, bands in the region 12500 cm^{-1}-12562 cm^{-1}, 26666 cm^{-1} and 32467 cm^{-1}-33333 cm^{-1} may be assigned to $^2B_{1g}\rightarrow{}^2A_1g$, $^2B_{1g}\rightarrow{}^2B_2g$ and CT bands respectively, corresponding to a distorted octahedral or tetragonal geometry [18,19,21,32,35-39].

Infrared spectra

The important IR data along with their assignments are presented in TABLE 4. The metal complexes under study did not show any band corresponding to free amino group; instead a new single sharp band appeared in the region 3100 cm^{-1}-3200 cm^{-1} (sometimes mixed with O-H) assignable to ν_{N-H} vibration [19,20,40,41] provide an evidence for the skeleton of the macrocyclic moiety. This was further supported by appearance of medium to strong intensity band at 1615 cm^{-1}–1651 cm^{-1} and 811 cm^{-1}-826 cm^{-1} attributed to N-H deformations coupled with N-H out of plane bending vibrations[41]. Medium to weak intensity bands at ~1175 cm^{-1} and 460 cm^{-1}-516 cm^{-1} may be assigned to C-N stretching vibration[19,42,43] and M-N stretching[16-18,44,45] respectively.

TABLE 4. **^{1}H-NMR Spectral Data (δ ppm) for the metal complexes in DMSO-d_6.**

Complex	Chemical shift, δ ppm
[CoL^{1}Cl$_2$]	1.65 (s, 2H, -NH-), 3.01 (t, 4H, -CH$_2$-S-), 3.18 (t, 4H, -CH$_2$-N-), 6.63^d and 7.58^d (16H, phenyl), 8.33 (s, 4H, OH)
[MnL^{1}Cl$_2$]	1.99 (s, 2H, -NH-), 2.96* (t, 4H, -CH$_2$-S-), 3.16* (t, 4H, -CH$_2$-N-), 6.49^d and 7.37^d (12H, phenyl), 9.68 (s, 4H, OH)
[CuL^{1}Cl$_2$]	2.10 (s, 2H, -NH-), 3.00 (t, 4H, -CH$_2$-S-), 3.18 (t, 4H, -CH$_2$-N-) 6.90^d and7.76^d (16H, phenyl), 8.11 (s, 4H, OH)
[CoL^{2}Cl$_2$]	1.87 (s, 2H, -NH-), 2.79 (t, 4H, -CH$_2$-S-), 2.93 (t, 4H, -CH$_2$-N-) 3.27 (s, 12H, phenyl -CH$_3$), 6.74^d, 7.34^d and 7.43^s (12H, phenyl), 8.9 (s, 4H, OH)
[MnL^{2}Cl$_2$]	1.78 (s, 2H, -NH-), 2.79* (t, 4H, -CH$_2$-S-), 3.12* (t, 4H, -CH$_2$-N-), 2.50* (s, 12H, phenyl -CH$_3$), 6.64^d, 7.20^d and 7.33^s (16H, phenyl), 8.02 (s, 4H, OH)
[CuL^{2}Cl$_2$]	2.03 (s, 2H, -NH-), 3.00 (t, 4H, -CH$_2$-S-), 3.13 (t, 4H, -CH$_2$-N-) 3.41 (s, 12H, phenyl -CH$_3$) 6.81^d, 7.57^d and 7.66^s (12H, phenyl), 8.18 (s, 4H, OH)
(s: Singlet, d: Doublet, t: Triplet, m: Multiplet); *Poorly resolved.	

New weak intensity bands supporting the formation of tellurium containing macrocyclic ring appear at 404 cm^{-1}-436 cm^{-1} due to Te-N vibrations [18-20,42-46]. Metal complexes show complete absence of the band at around 2400 cm^{-1} due to S-H vibrations. Two new medium intensity bands in the region 321 cm^{-1}-349 cm^{-1} and 755 cm^{-1}-763 cm^{-1} assigned to ν(M-S) and ν(C-S) vibrations respectively [16,44,47] are consistent with metal-sulfur co-ordination. Further, Nickel complexes show presence of medium to weak intensity bands in the region 302 cm^{-1}-331 cm^{-1} assigned to ν(M-Cl) vibration [16,44,48-50].

Proton magnetic resonance spectra

The proton chemical shifts for the metal complexes in DMSO–d$_6$ are presented in TABLE 4. Phenyl protons in the metal complexes resonate at slightly upfield side (6.49-7.76 δ ppm) as compared to the parent diaryltellurium dichlorides [26,27] due to replacement of 2 Cl by 2 nitrogen atoms and hence increase in electron density at the tellurium atom. 2-aminoethanthiol, $H_2N-CH_2-CH_2-SH$, exhibits proton chemical shifts at 1.45 (2H), 2.50 (1H), 2.75 (2H) and 2.87 (2H) δ ppm due to amino, thiol, methylene (adjacent to N) and methylene (adjacent to S) groups respectively [51,52].

A broad singlet in all the complexes at 1.65-2.10 δ ppm assignable to coordinated secondary amino group [16-18] confirms the formation of macrocyclic skeleton. Triplets in all the complexes at 2.95-3.07 and 3.12-3.19 δ ppm (slightly downfield side) may be assigned to (S-CH$_2$; 4H) and (N-CH$_2$; 4H) respectively, of the 2-aminoethanethiol moiety. All the above along with the absence of any band characteristic of NH$_2$ or SH protons, support the proposed macrocyclic framework.

Further, the independence of chemical shifts of aryl protons on the metal ions, hints at non-participation of Te atoms of the macrocycle in coordination with the metal ions. Thus, proton NMR studies support the formation of 10-membered tellurium containing dithiadiaza macrocycles and their quadridentate behavior as predicted by IR studies.

Based on elemental analyses, conductance, magnetic, infrared, electronic and proton magnetic resonance spectral studies, a distorted octahedral geometry involving two N and two S of the dithiadiaza macrocycle and 2 Cl may be proposed for these metal complexes (FIG. 1).

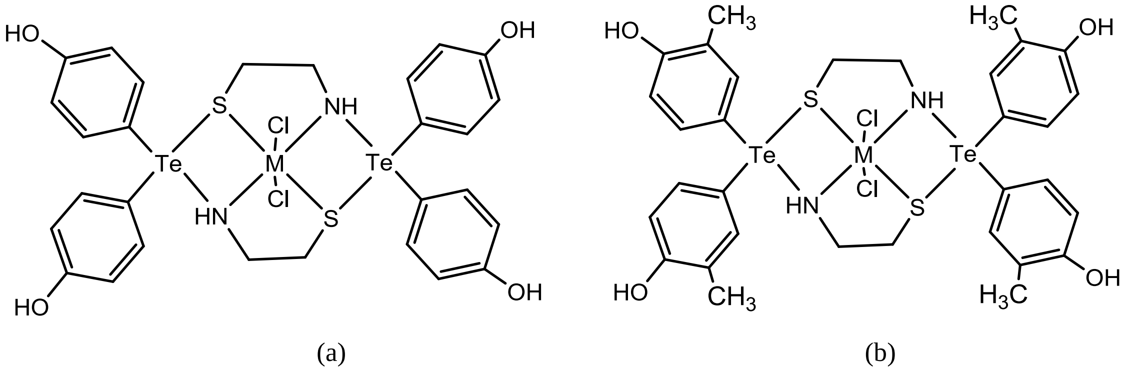

(a) (b)

FIG. 1. **Proposed structures of the metal complexes of the type (a) [ML^{1}Cl$_2$] and (b) [ML^{2}Cl$_2$]**

Antimicrobial results

The results are compiled in TABLES 5 and 6. MIC values indicate that the complexes possess moderate antimicrobial activity as compared to the standard bactericide (Cefadroxil) and fungicide (Fluconazole) but all the complexes show better antimicrobial activity than their precursors and thus indicated that complexation to metal enhances the activity of the ligand. The complex [MnL^{1}Cl$_2$] shows good activity against *C. albicans* (MIC=6.25) while [MnL^{2}Cl$_2$] is found to be most active against *E. coli* (MIC=6.25) and *C. albicans* (MIC=6.25).

TABLE 5. **Minimum Inhibitory Concentration (MIC) of the complexes against bacteria.**

Complex	**MIC (μg ml^{-1})**				
	Salmonella typhi	***Bacillus subtilis***	***Escherichia coli***	***Bacillus cereus***	***Staphylococcus aureus***
$NH_2(CH_2)_2SH$	12.5	12.5	25	12.5	12.5
R_2TeCl_2 (*p*-hydroxyphenyl)	25	25	25	25	25
R_2TeCl_2 (3-methyl-4-hydroxyphenyl)	25	25	12.5	25	25
[CoL^{1}Cl$_2$]	12.5	12.5	12.5	12.5	12.5
[MnL^{1}Cl$_2$]	12.5	12.5	12.5	12.5	12.5
[CuL^{1}Cl$_2$]	12.5	12.5	12.5	12.5	12.5
[CoL^{2}Cl$_2$]	12.5	12.5	12.5	12.5	12.5
[MnL^{2}Cl$_2$]	12.5	12.5	**6.25**	12.5	12.5
[CuL^{2}Cl$_2$]	12.5	12.5	12.5	12.5	12.5
Cefadroxil	3.12	1.56	3.12	1.56	3.12

TABLE 6. **Minimum Inhibitory Concentration (MIC) of the complexes against fungi.**

Complex	**MIC (µg ml^{-1})**		
	Aspergillus niger	***Aspergillus fumigatus***	***Candida albicans***
$NH_2(CH_2)_2SH$	12.5	12.5	25
R_2TeCl_2 (*p*-hydroxyphenyl)	25	25	25
R_2TeCl_2 (3-methyl-4-hydroxyphenyl)	25	25	12.5
$[CoL^1Cl_2]$	12.5	12.5	12.5
$[MnL^1Cl_2]$	12.5	12.5	**6.25**
$[CuL^1Cl_2]$	12.5	12.5	12.5
$[CoL^2Cl_2]$	12.5	12.5	12.5
$[MnL^2Cl_2]$	12.5	12.5	**6.25**
$[CuL^2Cl_2]$	12.5	12.5	12.5
Fluconazole	3.12	3.12	1.56

Conclusion

Co (II), Mn (II) and Cu (II) complexes have been synthesized by template condensation of diaryltellurium dichlorides with 2-aminoethanthiol in presence of metal chlorides and characterized by elemental analyses, molar conductance, electronic absorption, IR and ^{1}H NMR spectral studies. Based on these studies, a distorted octahedral structure has been assigned to these complexes. Some Mn (II) complexes show good antimicrobial activity against some pathogenic bacteria and fungi while others are moderately active.

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